

Evaluation of 3013 Can Pressurization Due to CO₂ and H₂O Desorption

Dan Kelly

Chemistry Division

Los Alamos National Laboratory



Evaluation Parameters

- Inner Can, Volume = 2266 ml
 - Mass PuO₂ = 5000 g
 - Specific Surf Area = 5 m²/g
 - Density of PuO₂ = 11.5 g/ml
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- Volume PuO₂ = 5000 g / 11.5 g/ml = 435 ml
 - Free Volume = 2266 – 435 = 1831 ml
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- 0.1 wt. % CO₂ = 5 g = 0.114 moles
 - 0.1 wt. % H₂O = 5 g = 0.278 moles



Pressure Evaluation

$$\cdot P_{CO_2, 0.1 \text{ wt. \%}, 250^\circ C} = nRT / V$$

$$= 0.114 \text{ mol} * 1206 \text{ psi, ml / K, mol} * 523 \text{ K} / 1831 \text{ ml} = 39.3 \text{ psi}$$

$$\cdot P_{H_2O, 0.1 \text{ wt. \%}, 250^\circ C} = 95.8 \text{ psi}$$

$\cdot P_{\text{inert packaging}} \sim 15 \text{ psi at RT (300 K)}$

$$\cdot P_{\text{inert, } 250^\circ C} = 15 \text{ psi} (523 \text{ K} / 300 \text{ K}) = 25.6 \text{ psi}$$

$\cdot \text{Total pressure of inert, 0.2 wt. \% CO}_2, 0.5 \text{ wt. \% H}_2\text{O}$

$$= 25.6 + 2(39.3) + 5(95.8) = 584 \text{ psi}$$



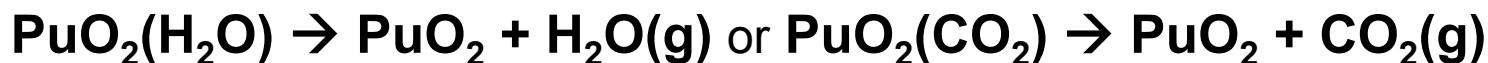
Kinetic Modeling Parameters

- $0.2 \text{ wt. \% CO}_2 = 2 (0.114) = 0.228 \text{ moles}$
- $0.5 \text{ wt. \% H}_2\text{O} = 5 (0.278) = 1.39 \text{ moles}$
- **1.618 total adsorbed moles (85.9 % H₂O, 14.1 % CO₂)**
- **Total Surface Area = $5000 \text{ g} * 5 \text{ m}^2/\text{g} = 2.5 \times 10^8 \text{ cm}^2$**
- **Assume 10.5 \AA^2 adsorption sites $\rightarrow 1.58 \times 10^{-9} \text{ moles of sites / cm}^2$**
- $1.58 \times 10^{-9} \text{ moles/cm}^2 * 2.5 \times 10^8 \text{ cm}^2 = 0.395 \text{ moles per adsorbed layer}$
- $1.618 \text{ moles} / 0.395 \text{ moles per layer} \sim 4.1 \text{ layers of adsorbate}$



Kinetic Modeling Parameters

- Model 4.1 layers of adsorbate (85.9 % H₂O, 14.1 % CO₂) assuming each layer has identical kinetics
- DESORPTION



Molecular Desorption Rate = $k \theta$, where

θ = coverage

$$k = v \exp(-E_{des} / RT)$$

$$E_{des, \text{CO}_2} = 25 \text{ kcal/mol}$$

$$E_{des, \text{H}_2\text{O}} = 10.4 \text{ kcal/mol} (= \Delta H_{vap, \text{H}_2\text{O}})$$

$$v = 10^{13} \text{ sec}^{-1}$$



Kinetic Modeling Parameters

- ADSORPTION



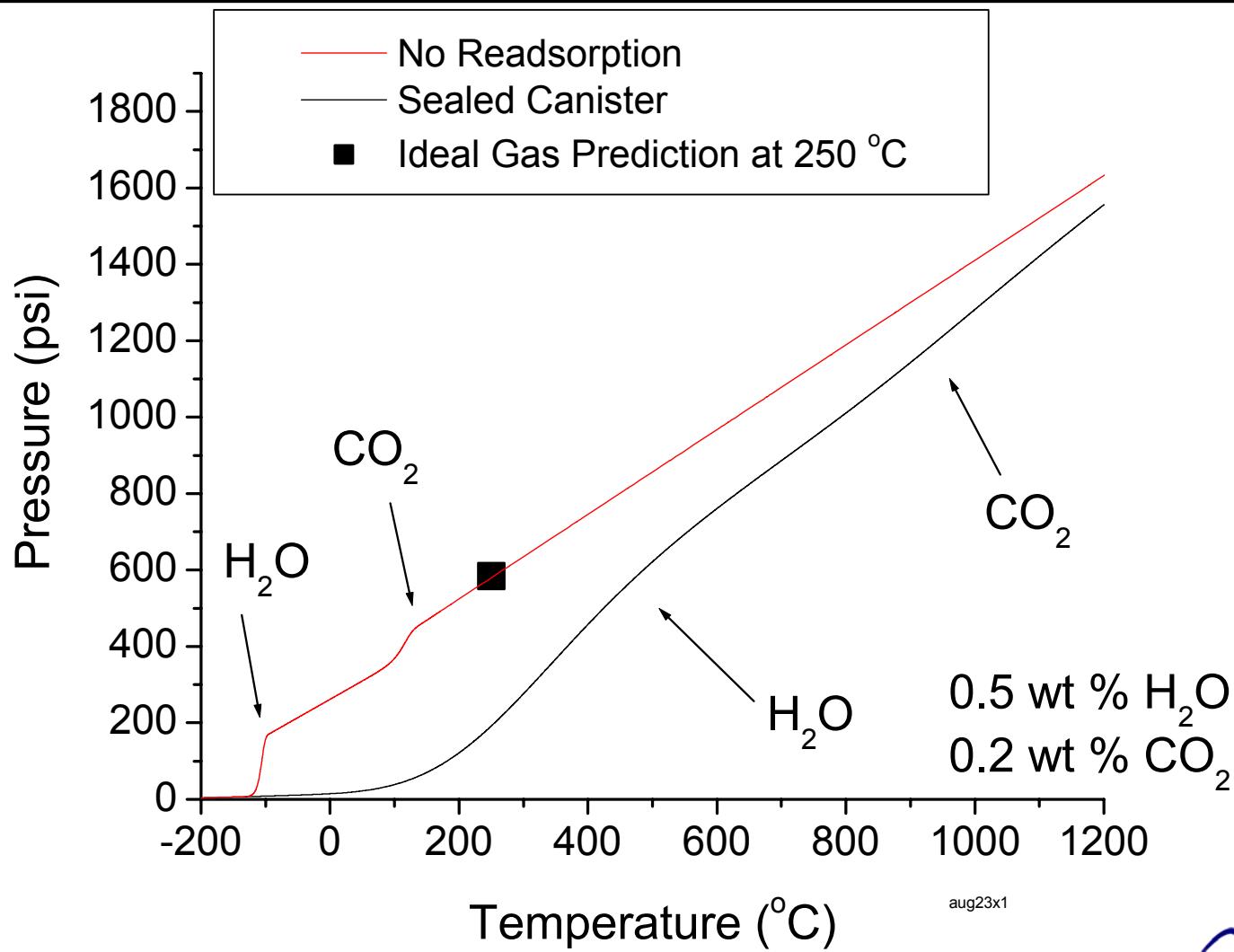
with a sticking coefficient (S) of 0.95 for H₂O and 0.25 for CO₂

TWO MODELING SCENARIOS

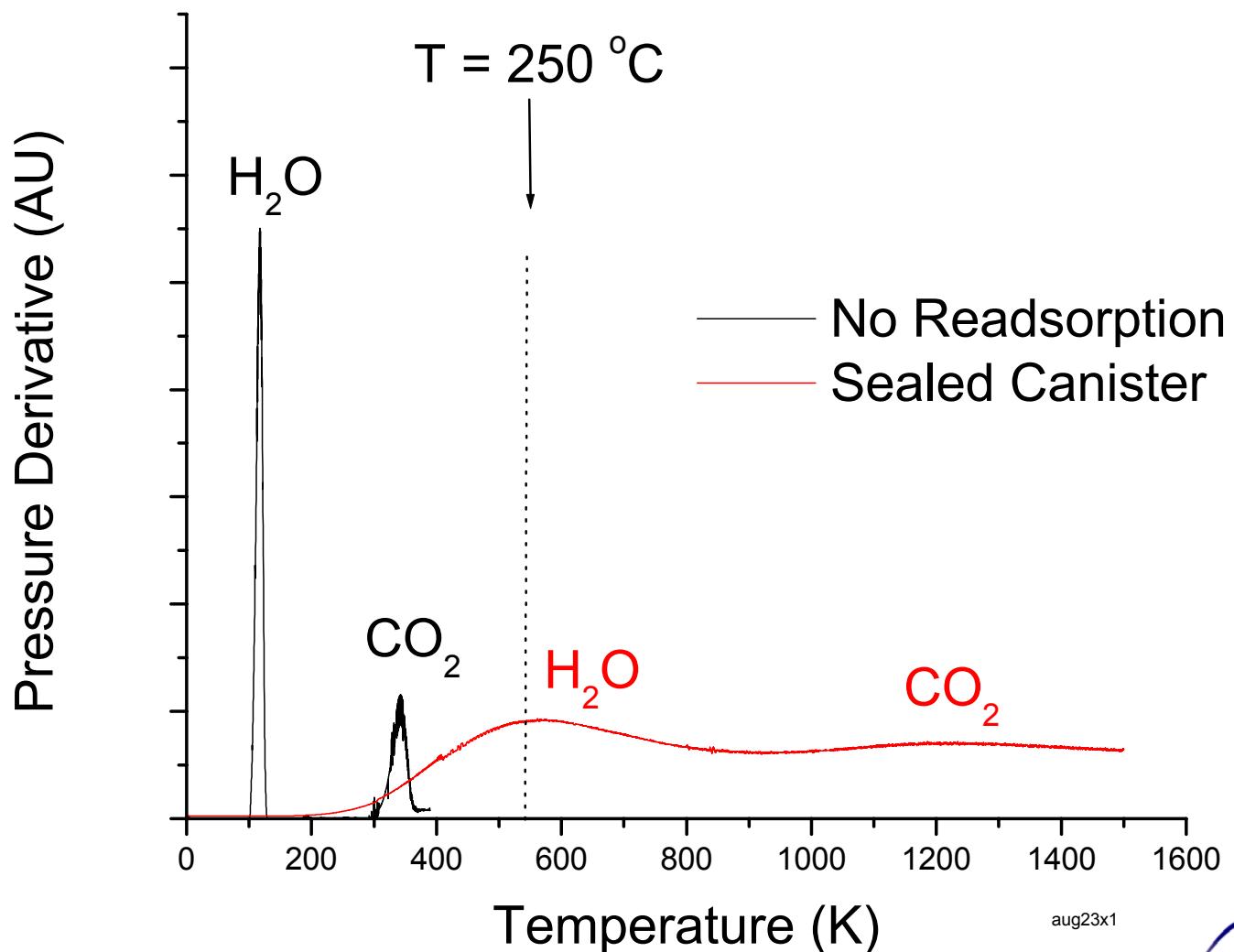
1. Readsorption is prohibited (S=0), such as flowing system (TGA) or ultrahigh vacuum thermal desorption. T_{des} will correspond to prediction by desorption theory and P determined by P = nRT/V (assuming all material desorbs). Not physically meaningful for sealed 3010 container.
2. Sealed system where readsorption takes place and T_{des} are higher. Meaningful for 3013 can where readsorption leads to lower pressures than calculated by ideal gas law.



Pressure vs. Can Temperature



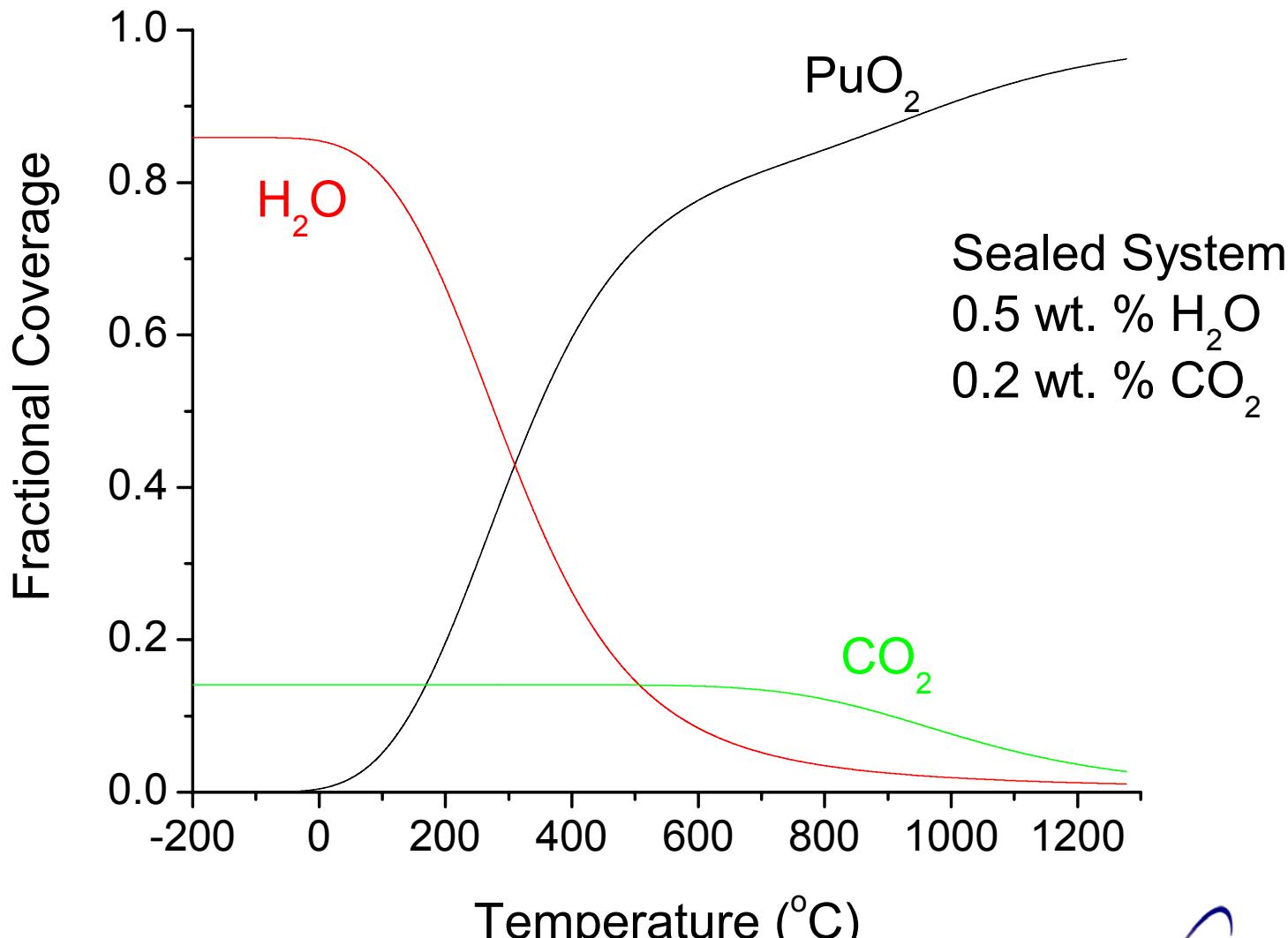
H_2O and CO_2 Desorption Peaks



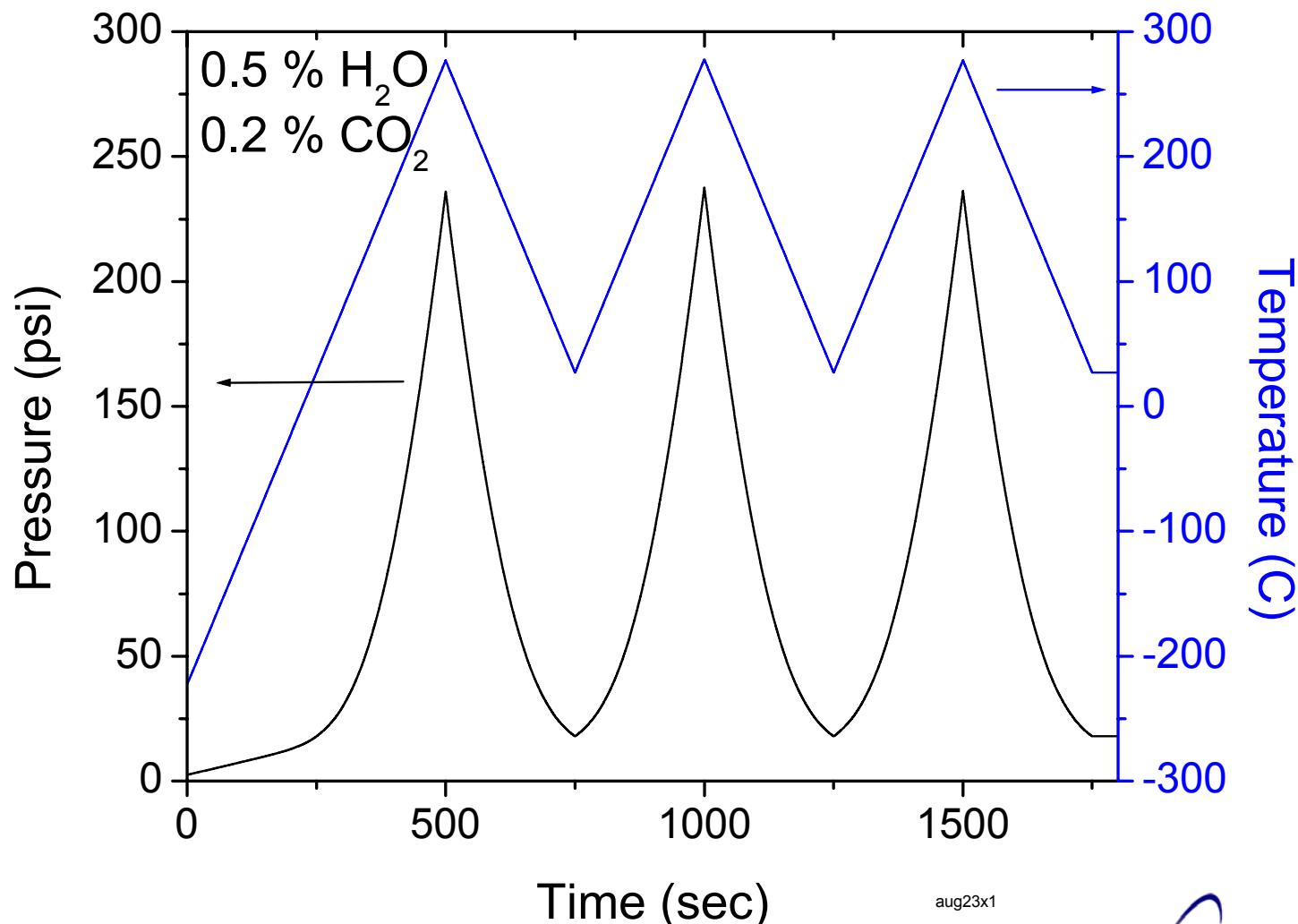
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Fractional Coverages



Pressure during Temperature Cycling Sealed System



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